References and Notes

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(3) Similar results have been obtained by anodic oxidation in acetonitrile containing fluoroboric acid as supporting electrolyte [E. Kotani, N. Takeuchi, and S. Tobinaga, *J. Chem. Soc., Chem. Commun.*, 380 (1973)].

(4) M. A. Schwartz, B. F. Rose, and B. Vishnuvajjala, *J. Am. Chem. Soc.*, **95**, 612 (1973).

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(6) E_{rev}(phenol) > E_{rev}(phenol ether) for phenols with not more than one *o*-alkyl substituent and E_{rev}(phenol) < E_{rev}(phenol ether) for 2,6-dialkylphenols.

(7) The diarylalkanes containing *tert*-butyl groups (**6** and **8**) looses one *tert*-butyl group in the presence of TFMS. Cyclic voltammograms run at various times after the preparation of a 1 mM solution of **6** in CH_2Cl_2–TFMS (1%) at −50 °C showed that the rate constant for this dealkylation is about $4 \times 10^{-4}\ s^{-1}$ under these conditions. In a preparative oxidation of **6** in CH_2Cl_2–TFMS at −50 °C, compound **35** was obtained in 60% yield with 100% conversion (two stereoisomeric spirodienones should be obtained from the diarylpropane with one *tert*-butyl group. However the same product (**35**) is formed by dienone-phenol rearrangement of these spirodienones). From this we conclude that **35** is formed by cyclization of the mono-*tert*-butyl compound.

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(10) This appears a reasonable assumption since our measurements in CH_2Cl_2–FSO_3H (ref 5) have shown that the oxidation potential for the oxidation of a cation radical of a phenol or a phenol ether is at least 300–400 mV more anodic than the oxidation potential for the oxidation of the phenol or phenol ether to the cation radical. Preparative experiments (Table III) were carried out at the latter potential.

(11) In our preliminary communication (ref 2) we argued on the basis of the difference in oxidation potential between a phenol and its methyl ether that the initial one-electron transfer from a phenol to an anode with formation of a cation radical is generally followed by rapid deprotonation to a phenoxy radical which can dimerize (path e in Scheme I), react as an electrophile (path d), or become further oxidized to a phenoxonium ion (path f). Our finding (ref 5) that the reversible potential (in CH_2Cl_2–FSO_3H) for the redox reaction

$$\text{phenol} \underset{+e}{\overset{-e}{\rightleftharpoons}} \text{phenol cation radical}$$

is about the same as for the reversible redox reaction (also in CH_2Cl_2–FSO_3H),

$$\text{phenol ether} \underset{+e}{\overset{-e}{\rightleftharpoons}} \text{phenol ether cation radical}$$

of the corresponding methyl ether supports this hypothesis.

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Dimer Formation during Reactions of Benzylic Halides with Lithium Naphthalene and Mechanisms of Dimer Formation from Reactions of Benzylic Halides with Benzylic Carbanions

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Abstract: Reactions of benzylic fluorides and chlorides with lithium naphthalene in THF have been found to give dimers in 61–79% yields. Competition experiments using equimolar benzhydryl and benzyl chlorides with lithium naphthalene produced three possible ethane dimers in the statistically expected ratio of 1:2:1. Diphenylmethyllithium competition experiments using an excess of equimolar benzhydryl and benzyl chlorides produced equal amounts of *sym*-tetraphenylethane (**1**) and 1,1,2-triphenylethane (**2**) in fast reactions. Conversely, equimolar benzhydryl and benzyl fluorides reacted slowly with diphenylmethyl carbanion to produce **2** and **1** in unequal amounts (2:1 = 1.92). The large difference in reaction rate between benzylic chlorides and fluorides in reactions with benzylic carbanions together with the failure of trityl and benzhydryl fluorides to react with trityl carbanion have led to the suggestion that benzylic fluorides do not react with benzylic carbanions by an electron-transfer mechanism to produce dimers via a geminate radical pair intermediate. The failure of competition experiments between lithium naphthalene and equimolar trityl and benzhydryl fluorides to form significant amounts of pentaphenylethane was interpreted as evidence against dimer formation through a radical coupling pathway. Comparison of benzylic halide–lithium naphthalene reactions with benzylic halide–benzylic carbanion reactions indicates that dimer formation in aromatic radical anion reactions proceeds through a carbanion intermediate but follows two different mechanisms depending upon which halide is reduced. Benzylic chlorides react with their counterpart carbanions to yield dimers rapidly via an electron-transfer mechanism having a geminate radical pair intermediate whereas fluorides appear to react slowly by a classical displacement mechanism.

The reactions of alkyl halides with alkali metal naphthalenes have been studied intensively during the past 10 years.[1-8] There is general agreement that this aromatic radical anion reduces the halide by dissociative electron transfer to produce an organic radical and a halide anion via eq 1.[10] The alkyl radicals appear in part as an alkylation product of naphthalene and as simple reduction products, RH, or alkyl dimers, R–R. Substantial efforts have been devoted

Table I. Polyphenylethane Yields from Titrimetric Addition of Lithium Naphthalene to an Equimolar Mixture of Benzhydryl and Benzyl Chlorides

Temp, °C	Ph_2CH-$CHPh_2$ (**1**, STP),[a] %	Ph_2CH-CH_2Ph (**2**, TPE),[b] %	$PhCH_2$-CH_2Ph (**3**, BB),[b] %
Ambient	23	49	24
Ambient	24	49	24
−78	24	48	26

[a] By isolation. [b] By quantitative GC using a 6-ft 10% Carbowax 20M on Chromosorb W-DMCS treated column using a Hewlett-Packard 5750 B instrument with a Disc integrator. Ph_3CH was the internal standard.

to the questions of the mechanisms by which these products form.[3,4,7b]

$$R\text{-}X + M\text{-}C_{10}H_8 \rightarrow R\cdot + X^- + C_{10}H_8 \quad (M = Li, Na, K \ldots.) \qquad (1)$$

At first, competition experiments were interpreted in terms of radical coupling ($2R\cdot \rightarrow R$-R) to explain alkyl dimer formation.[2a] Later this view was challenged[2d,e] because of the failure of 1,4-diiodobutane to form halogen containing *n*-octanes, or indeed *n*-octane itself,[4] as well as on the basis of carbanion trapping experiments with $MgBr_2$.[2e]

A two-step mechanism shown in eq 2 for alkyl dimer formation was discarded[4] because sterically hindered neopentyl iodide reacts rapidly with sodium naphthalene to give bineopentyl in 70% yield, and such sterically hindered halides do not react rapidly in SN2 reactions.[2a,b]

$$RX \xrightarrow{C_{10}H_8Na} R\cdot \xrightarrow{C_{10}H_8Na} R{:}^- \xrightarrow[S_N2]{R\text{-}X} R\text{-}R \qquad (2)$$

The best explanation for the rapid rates of alkyl dimer formation from alkyl halides is the geminate radical pair proposal of eq 3.[2d,7b]

$$RNa + RX \rightarrow [R \cdot R \cdot NaX] \rightarrow R\text{-}R \qquad (3)$$

It assumes that carbanions are generated in two rapid steps by electron transfers from radical anion as seen in eq 2 and that eq 3 replaces the SN2 displacement step of eq 2.

The geminate radical pair (or caged radicals) proposal easily explains competition experiment data[2a,6] (see below) and finds experimental support from the electron-transfer oxidation of triphenylmethyl carbanion by triphenylmethyl chloride.[6]

Now we wish to contrast dimer formation from benzylic halide–benzylic carbanion reactions with dimer formation from benzylic halide–lithium naphthalene reactions. In addition we infer from competition experiments with benzylic chlorides that the radical pair hypothesis applies while benzylic fluorides appear to follow a carbanion displacement mechanism.

Results

Treatment of 1 equiv of an equimolar mixture of benzhydryl and benzyl chlorides with 1 equiv of lithium naphthalenide in tetrahydrofuran (THF) by slow titrimetric addition produced bibenzyl (**3**), 1,1,2-triphenylethane (**2**), and *sym*-tetraphenylethane (**1**) in a ratio of 1:2:1 as shown in Table I.

Treatment of 2 mol of an equimolar mixture of benzhydryl and benzyl chlorides in THF with 1 mol of diphenylmethyllithium at 25 °C produced equal amounts of **1** and **2** as judged by quantitative VPC analysis. The isolated yields of **1** and **2** were 97 and 95%, respectively. Although careful kinetic studies have not been run, the rates of formation of **1** and **2** are high in that 0.01 mol each of **1** and **2** form within 3–5 min in 0.150 l. of solvent. An instantaneous disappearance of the red carbanion color occurs.

Table II. Reactions of Benzylic Fluorides with Lithium Naphthalene in THF at 25 °C

Compd	Mole ratio ArH/R-F	RF added to Li-$C_{10}H_8$		Li-$C_{10}H_8$ added to R-F	
		% R-R	% RH	% R-R	% R-H
Ph_3C-F	1	4[a,c]	90[b]	2[a,c]	95[b]
Ph_2CH-F	1	70[a]	22[b]	79[a]	15[b]
$PhCH_2F$	1	61[b]	30[b]	71[b]	20[b]

[a] By isolation. [b] By quantitative gas chromatography; all experiments run in duplicate. [c] *p*-Benzhydryltetraphenylmethane.

Table III. Reaction of Benzylic Carbanions (Li^+) with Benzylic Halides in THF at Room Temperatures

Carbanion	Halide	Reaction time	Product	% isolated yield R-R
$Ph_3C{:}^-$	Ph_3C-F	2 days	*d*	5
$Ph_3C{:}^-$	Ph_2CH-F	6 days	NR[c]	0
$Ph_3C{:}^-$	$PhCH_2$-F	4.75 h[a]	PH_3CCH_2Ph	91
$Ph_2CH{:}^-$	Ph_2CH-F	1 h[a]	Ph_2CH-$CHPh_2$	96
$PhCH_2{:}^-$	$PhCH_2$-F	20 min[a,e]	$PhCH_2$-CH_2Ph	95
$Ph_3C{:}^-$	Ph_2CH-Cl	15 min[b]	Ph_3C-$CHPh_2$	91
$Ph_3C{:}^-$	$PhCH_2$-Cl	15 min[b]	Ph_3CCH_2Ph	95
$Ph_2CH{:}^-$	Ph_2CHCl	15 min[b]	$Ph_2CHCHPh_2$	100.0

[a] Time to decolorization of carbanion color after completion of mixing. [b] Addition time of halide to carbanion; decolorization occurs upon completing of addition. [c] Three tries. [d] *p*-Benzhydryltetraphenylmethane. [e] This reaction was run in ether.

$$\underset{0.02\ \text{mol}}{Ph_2CH{:}^-} + \underset{0.02\ \text{mol}}{Ph_2CHCl} + \underset{0.02\ \text{mol}}{PhCH_2Cl} \xrightarrow[25\ ^\circ C]{THF} \underset{0.01\ \text{mol}}{\mathbf{1}} + \underset{0.01\ \text{mol}}{\mathbf{2}} \qquad (4)$$

A similar reaction of an equimolar mixture of benzhydryl and benzyl chlorides in THF with 1 mol of triphenylmethyl carbanion at 25 °C produced equal amounts (0.01 mol) of *unsym*-tetraphenylethane and pentaphenylethane within 2.0 min.

Reactions of benzylic fluorides with lithium naphthalene also produced dimers and reduction products as shown in Table II. The yield of dimer is slightly higher if one adds the lithium naphthalene solution to the halide solution.

In Table III are summarized some reactions of benzylic carbanions in THF at ambient temperatures with benzylic fluorides and chlorides. Two factors must be noted. The first is that the benzylic fluorides react much slower than their chloride counterparts in dimer formation. The second is that trityl carbanion does not react with benzhydryl fluoride at all and only marginally with trityl fluoride.

In contrast to the radical anion competition experiments with benzhydryl and benzyl chlorides, treatment of an equimolar solution of 1 mol of benzhydryl and benzyl fluorides with 1 mol of lithium naphthalene produced **1**, **2**, and **3** in a ratio of 23.6:68.2:8.2 (±1.1%).

When diphenylmethyl carbanion competition experiments were run with a twofold molar excess of equimolar benzhydryl and benzyl fluorides, the ratio of **2** to **1** was 1.92.

A competition experiment between 1 mol of lithium naphthalene and 1 mol of equimolar trityl and benzhydryl fluorides gave 27% STP (**1**) and less than 2% of pentaphenylethane.

Discussion

The formation of dimers **1**, **2**, and **3** in the competition experiments of Table I in a statistical 1:2:1 distribution could be interpreted either in terms of a simple radical coupling mechanism,[2a] or by an electron-transfer process in which geminate radical pair intermediates are formed.[3,4,7] A carbanion mechanism involving an SN2 displacement step for dimer formation would be expected to give unequal amounts of **1**, **2**, and **3** because dimer formation rates should be sensitive to steric effects and the difference in nucleophilicity of the intermediate carbanions.

The formation of equal amounts of STP (**1**) and TPE (**2**) in the reaction of benzhydryl carbanion with an excess of equimolar benzhydryl and benzyl chlorides appears to be best interpreted in terms of the electron-transfer mechanism via a geminate radical pair intermediate. That no radicals escape from the radical pair cages can be seen by the complete absence of cross coupling dimer (**3**) among the products.

One could invoke a carbene mechanism[12] for dimer formation in which an organolithium carbanion abstracts an α-hydrogen atom from benzyl chloride or benzhydryl chloride. α elimination in a second step generates the carbene which inserts in any convenient carbon-lithium bond, including that of the immediate precursor to the carbene. For this mechanism to explain the data, one has to explain why trityl carbanion cannot abstract the methinyl proton of benzhydryl fluoride but can deprotonate benzyl fluoride (see Table III).

Evidence for carbene intermediates in sodium naphthalene reductions of geminal dihalides was sought by Sargent who found carbene radical anion intermediates to be more plausible than a free carbene or carbenoid.[13]

Another possible explanation of the dimer-forming step might be radical attack on a carbanion (eq 5). Such a radical-nucleophile combination reaction step was hypothesized for the electron-transfer mechanism for replacement of aryl iodine atoms from aryl iodides with amino groups during potassium in liquid ammonia reactions that contained amide ion.[14]

$$R\cdot + R:^- \rightarrow R\text{-}R + e^- \qquad (5)$$

While such a mechanism as eq 5 may be the pathway for dimer formation during lithium naphthalene reductions of benzylic halides, it cannot be the operating process in the carbanion competition experiments because no cross coupling dimer (**3**) is found among the products.

In contrast with reports of 0% dimer formation in reactions of sodium naphthalene with simple alkyl fluorides, benzhydryl and benzyl fluorides give 61–79% yields of ethane dimers using lithium naphthalene.

The reasons for this difference can now be understood in terms of the failure of alkyl fluorides to form dimers rapidly by the electron-transfer mechanism coupled with the known instability of organo sodium carbanions in ether solvents.[1]

Although literature rate data show that radical production from fluorides is slower than from chlorides[7a] and chlorides < bromides < iodides,[8] reactions of the benzylic fluorides with lithium naphthalene still appear to be fast on the laboratory time scale. The observable differences between benzylic fluorides and chlorides in the titrimetric addition of lithium naphthalene is that in the benzylic fluorides one sees the instantaneous formation of the red carbanion which then disappears slowly in the dimer-forming reaction.[15] As a titration proceeds and the solution becomes depleted in [RF], the carbanion color persists longer. This analysis is confirmed by the noticeably slower dimer formation in Table III where authentic benzylic carbanions of known concentration react with benzylic fluorides.

The failure of trityl carbanion to react with trityl fluoride or benzhydryl fluoride to give dimers is significant because it means that neither of these benzylic fluorides can oxidize the carbanion by an electron-transfer mechanism unlike their chloride counterparts.[6] The fact that trityl carbanion *slowly* reacts with benzyl fluoride to produce dimer suggests that a classical displacement mechanism rather than the faster electron-transfer mechanism is the pathway for dimer formation from benzylic fluorides.

Not only is this hypothesis suggested by the qualitative rate data, it is also in harmony with the benzhydryl carbanion competition experiment in which benzhydryl carbanion reacts faster with benzyl fluoride to form TPE (**2**) than with benzhydryl fluoride to form **1**.

The isolation of 2–4% of *p*-benzhydryltetraphenylmethane from trityl fluoride in Table II indicates the maximum possible amount of α-para coupling of trityl radical that can compete with electron-transfer reduction of radicals to trityl carbanions. The finding in Table III that trityl carbanion reacts slowly with trityl fluoride to give 5% of *p*-benzhydryl–tetraphenylmethane tends to negate the possibility that this dimer formed by coupling of radicals.

Since the slow dropwise addition of lithium naphthalene to equimolar trityl and benzhydryl fluorides produced no isolable (or NMR detectable) amount of pentaphenylethane (i.e., cross coupling product), it is very unlikely that ethane dimers generated by means of alkali metal aromatic radical anions reacting with fluorides are forming via α coupling of benzylic radicals.

Until quite recently, hypotheses of radical generation via eq 1 did not contemplate the possibility of an alkyl halide radical anion precursor $[RX]\cdot^-$ to radicals, eq 6.[16] Now the slower rate of fluoride cleavage from hexyl fluoride compared with hexyl chloride with sodium naphthalene has led to the hypothesis of a later transition state for fluoride departure.[16] Even if $RF\cdot^-$ is an intermediate, our competition experiment data cannot show whether the rates of radical generation (and hence the rates of carbanion formation) would be sensitive to organic structure because the rates of dimer formation from carbanions and alkyl fluorides are very much slower than the steps leading up to the carbanion generation.

$$MC_{10}H_8 + RF \rightarrow M^+(RF\cdot^-) + C_{10}H_8 \rightarrow R\cdot \qquad (6)$$
$$M = Li, Na\ldots$$

In the preliminary communication to this paper,[6] we interpreted the formation of dimer **1** from benzhydryl chloride during the slow dropwise addition of lithium naphthalene as occurring by the α coupling of two benzhydryl radicals. From the present competition experiments, it is not possible to distinguish this mechanism from the geminate radical pair mechanism for dimer formation. However, study of recent literature reports[18,19] of dimer formation via coupling of benzylic radicals obtained by photolysis of benzylic azoalkanes shows that α-para coupling of cumyl radicals occurs and in two systems accounts for 40 and 10–20% of the dimers formed. A third system involves para attack of hexafluorocumyl radical by benzyl radical.[19] If such α-para coupling products form in the addition of lithium naphthalene to benzhydryl chloride (or bromide), the maximum potential yield is 4%.[6] This fact together with the very fast reactions of benzylic carbanions with benzylic chlorides and bromides to form ethane dimers causes us to be skeptical of our earlier interpretation of dimer formation through a radical-coupling mechanism.

This statement is made in spite of our successful ESR detection of the 3,3′,5,5′-tetra-*tert*-butylbenzhydryl radical.[10] It remains to be shown whether the fate of the radical in such flow system experiments where $[RBr]_i = 7 \times 10^{-3}$ M. is dimer formation. Preparatively, 3,3′,5,5′-tetra-*tert*-butylbenzhydryl bromide reacts with lithium naphthalene to give 72% of the ethane dimer.[20]

Summary and Conclusions

A large rate difference for ethane dimer formation in reactions between benzylic fluorides and chlorides with benzylic carbanions together with similar rate differences in competition experiments has led us to propose that benzylic fluorides cannot react by an electron-transfer mechanism to give dimers.

Comparison of dimer formation in carbanion reactions with that found in aromatic radical anion reactions with benzylic halides confirms that a carbanion intermediate is the precursor to the ethane dimer.

Aromatic radical anion competition experiments with equimolar mixtures of benzylic chlorides have been interpreted as supporting the formation of a geminate radical pair.[2d,7]

Competition experiments using trityl and benzhydryl fluoride have been interpreted against the possibility that dimer formation occurs by the α coupling of radicals.

Experimental Section

Gas chromatography analyses were performed with a Hewlett-Packard 5750 B instrument equipped with a H_2 flame-ionization detector, a thermal conductivity detector, and Disc integrator. Column diameters are ⅛ in., and the lengths were 6 ft. Three different packings were used: (1) 10% SE 30 on Chromosorb W-DMCS; (2) 20% poly(phenyl ether) (5 ring) on Chromosorb W-DMCS; (3) 10% Carbowax 20 M on Chromosorb W-DMCS.

NMR spectra were obtained on a Varian A-60A, T-60, or HA-100 spectrometers.

All reactions were performed under an argon atmosphere using reagents purified, prepared, or analyzed as described below.

Naphthalene, Eastman Kodak Co., White Label, was dried in vacuo over anhydrous $CaCl_2$.

Triphenylmethane, Eastman Kodak Co., White Label, was recrystallized from hexane and dried in vacuo.

Diphenylmethane, Matheson Coleman and Bell, was distilled in vacuo, bp 120–121 °C at 9 mm, and stored over Linde 4-A molecular sieves.

Lithium wire, ⅛ in. diameter from Matheson Coleman and Bell, was stored under light mineral oil and was washed twice with THF prior to use.

Tetrahydrofuran, Baker Analyzed, was distilled from fresh lithium aluminum hydride. Benzophenone and sodium metal were added to the distillate and the resulting ketyl was refluxed for 24 h. The solvent was distilled from the ketyl before use.

Alkyllithiums, Alfa Inorganics, were titrated prior to use by the procedure of Eastham.[21]

Benzyl fluoride, Pierce Chemical Co., was distilled prior to use, bp 140 °C at atmospheric pressure.

Triphenylmethyl fluoride, Cationics Inc., was used without further purification, mp 103–104 °C.

Silver fluoride, Cationics Inc., was used as secured.

Lithium naphthalene was prepared as follows: In a preflamed flask having a dry argon atmosphere were placed naphthalene (5.00 g, 0.039 mol), dry THF (100 ml), and Li wire (0.270 g, 0.039 mol). The wire had been flattened and cut into thin slices. The green color of the radical anion appeared within 15–30 s, and the solution was stirred for 1.5 h to allow complete solution of the metal.

Benzyllithium was prepared as follows: Benzyl methyl ether (13.3 g, 0.108 mol) was added dropwise to a rapidly stirred mixture of ethyl ether (250 ml) and Li wire (5 g), which had been flattened and cut into thin slices. The straw-colored mixture was stirred for 2 h, after which a straw-colored material settled, leaving a bright red solution of benzyllithium. The benzyllithium solution was separated from excess Li and precipitate either by pumping through a glass tube having a loose glass wool plug using argon, or by means of a gas-tight syringe (100 ml) fitted with a needle.

Benzhydryl fluoride was prepared as follows: Benzhydryl bromide (49.4 g, 0.2 mol) in 100 ml of dry acetonitrile was treated with AgF (38 g, 0.3 mol) suspended in 150 ml of CH_3CN. The exothermic reaction was maintained between 20 and 40 °C by addition of the AgF solution portionwise during 20 min. After 2 h, AgBr was filtered, and the organic layer was washed four times with distilled H_2O and dried over Na_2SO_4. Excess CH_3CN was distilled, and the remaining organic material was distilled in vacuo to give 18.7 g, 50%, of benzhydryl fluoride, bp 110–113 °C at 1 mm: NMR ($CDCl_3$) δ 6.4 (d, 1 H), $J_{H\text{-}F} = 48$ Hz, 7.3 (m, 10 H).

Anal. Calcd for $C_{13}H_{11}F$: C, 83.81; H, 5.91; F, 10.21. Found: C, 83.72; H, 6.02; F, 10.33.

Although solvolysis rate studies on benzhydryl fluoride have been published,[22] details on the preparation and physical properties of this compound may be recorded in the Ph.D. thesis of R. B. Mosely, Massachusetts Institute of Technology, July 1952. The compound can be stored in polyethylene bottles and kept in a refrigerator for as long as 4 months.

Addition of Lithium Naphthalene to an Equimolar Mixture of Benzyl Chloride and Benzhydryl Chloride. To an equimolar mixture of benzyl chloride (0.01 mol) and benzhydryl chloride (0.01 mol) was added dropwise lithium naphthalene (0.02 mol). The reaction mixture was stirred for an hour before quenching with H_2O (10 ml). Extraction with 100 ml of ether, drying over sodium sulfate, and then removal of the solvent afforded a white reaction mixture. Treatment of this mixture with the minimum amount of hot benzene for dissolution and cooling to room temperature afforded 0.40 g (24%) of *sym*-tetraphenylethane.

Analysis by NMR spectroscopy and then by GC afforded 24% of bibenzyl and 49% of 1,1,2-triphenylethane.

The above experiment was carried out three times, twice at ambient temperature and at −60 °C, with no appreciable differences in the yields.

Reaction of Diphenylmethyllithium with an Equimolar Mixture of Benzyl Chloride and Benzhydryl Chloride. A solution of the titled halides (0.02 mol each) in 50.0 ml of THF was added in one portion to diphenylmethyllithium (0.02 mol, in 100 ml of THF) at 25 °C. After decoloration (20 min), 3 ml of distilled water was added. Addition of ether (100 ml) and water (50 ml) was followed by drying of the ether layer (Na_2SO_4). Removal of the solvent with a rotary evaporator, followed by recrystallization from benzene gave 3.34 g of *sym*-tetraphenylethane (0.00971 mol, 48.5%, mp 218–219 °C. Evaporation of the benzene, followed by recrystallization from ethanol, gave 2.50 g of 1,1,2-triphenylethane (0.00969 mol, 48.5%, mp 52–54 °C). Both hydrocarbons exhibited spectral and physical properties that are identical with literature data.[23]

Run 2: A nearly identical experiment was run with the exception that 0.04 mol of diphenylmethyllithium was used. Again 50% of the carbanion reacted with benzyl chloride and 50% with benzhydryl chloride showing that the rates of dimer formation are equal and independent of organic structure.

Reaction of Triphenylmethyllithium with an Equimolar Mixture of Benzyl Chloride and Benzhydryl Chloride. A THF (50 ml) solution of benzyl chloride (0.02 mol) and benzhydryl chloride (0.02 mol) was added in one portion to 0.267 M triphenylmethyllithium (75 ml). Decolorization was instantaneous and water (50 ml) was added 2.0 min after mixing. Extraction with ether and drying over Na_2SO_4 was followed by removal of the ether in the rotary evaporator. Treatment of the crude mixture with 30 ml of petroleum ether gave 3.30 g of *unsym*-tetraphenylethane (0.00959 mol, 48.0%, mp 143–144 °C). Evaporation of the petroleum ether, followed by solution in the minimum amount of hot benzene and addition to 100 ml of absolute ethanol, afforded pentaphenylethane (4.00 g, 0.00976 mol, 48.8%, mp 158–161 °C).[6,24,25]

Addition of Trityl Fluoride to Lithium Naphthalene. Trityl fluoride (5.24 g, 0.02 mol) in THF (50 ml) was added dropwise to 0.02 mol of lithium naphthalene in 100 ml of THF. After completion of the addition, the solution turned a red color and remained red for 48 h until quenched with 10 ml of H_2O.

The reaction mixture was treated with 100 ml of saturated NH_4Cl, extracted into 100 ml of ether, and the organic layer was dried (Na_2SO_4). Removal of the solvent, followed by trituration with 50 ml of hexane, gave 0.45 g (4%) of *p*-benzhydryltetraphenylmethane, mp 226–227 °C. The mother liquor contained triphenylmethane and trityl fluoride.

Reaction of Benzhydryl Fluoride with Lithium Naphthalene. Benzhydryl fluoride (5.58 g, 0.03 mol) in THF (50 ml was added dropwise to 0.39 M lithium naphthalene (0.039 mol). After stirring 1.5 h, the green color of lithium naphthalene disappeared. Addition of H_2O (100 ml), extraction with ether (100 ml), drying over Na_2SO_4, and removal of solvent gave a white solid which was recrystallized from benzene and identified as *sym*-tetraphenylethane (3.51 g, 70%, mp 218–219 °C: NMR ($CDCl_3$) δ 4.8 (s, 2 H), 7.1 (m, 20 H). Quantitative analysis of the mother liquor by gas chromatography (6-ft column, 10% SE 30/Chromosorb W, 150 °C) gave 22% of diphenylmethane.

Reaction of Benzyl Fluoride with Lithium Naphthalene. To 0.39 M lithium naphthalene in THF (100 ml) was added dropwise benzyl fluoride (0.039 mol in 50 ml of THF). After addition of the fluoride, 30 min of stirring were required for complete decoloration of the green solution. Analysis of the reaction mixture by gas chromatography (6 ft, 10% SE 30/Chromosorb W, 150 °C) showed bibenzyl (2.18 g, 61.%) and toluene (1.08 g, 30%).

Triphenylmethyllithium and Diphenylmethyllithium. To a solution of triphenylmethane (0.02 mol) or diphenylmethane (0.02 mol) in 100 ml of THF under argon at 0 °C was added *n*-butyllithium (0.021 mol, Alfa Inorganics). The solutions were allowed to stir for 1.0 h (3.0 h for Ph_2CH_2) before use. The coupling product yields shown in Table III demonstrate that metalation yields exceeded 91% for both diphenylmethane and triphenylmethane.

Reaction of Diphenylmethyllithium with an Equimolar Mixture of Benzyl Fluoride and Benzhydryl Fluoride. A THF (50 ml) solution of benzyl fluoride (0.01 mol) and benzhydryl fluoride (0.01 mol) was added in one portion to diphenylmethyllithium (0.01 mol) in THF (100 ml) at 0 °C. After stirring for 5 min decolorization occurred. Analysis of the organic layer by quantitative gas chromatography showed 67% of 1,1,2-triphenylethane and 34% *sym*-tetraphenylethane.

Addition of Trityl Fluoride to Trityllithium. To 0.2 M trityllithium in THF (100 ml) was added trityl fluoride (5.24 g, 0.02 mol) in THF (50 ml). After stirring 48 h, the red color of the carbanion began to fade away. Hydrolysis with brine (100 ml), extraction with ether (3 × 50 ml), and drying over Na_2SO_4 was followed by solvent distillation. As the solvent was being removed, *p*-benzhydryltetraphenylmethane precipitated (0.5 g, 5%, mp 226–227 °C). The remaining mother liquor contained triphenylmethane and trityl fluoride (95% recovery).

Addition of Benzhydryl Fluoride to Trityllithium. To 0.2 M trityllithium in THF (100 ml) at 0 °C benzhydryl fluoride (3.72 g, 0.02 mol) was added in one portion. After 6 days the red color persisted and work-up as described above for trityl fluoride produced an oil which was a mixture of triphenylmethane, benzhydryl fluoride, and reduction and solvolysis products of the fluoride.

Reaction of Benzyl Fluoride with Trityllithium. To 0.2 M trityllithium in THF (100 ml) benzyl fluoride (2.20 g, 0.02 mol) in THF (15 ml) was added dropwise during 15 min. The reaction was stirred at ambient temperature for 4.75 h when the red color of the carbanion disappeared. Addition of water (100 ml), extraction with ether (2 × 50 ml), drying of the ether phase (Na_2SO_4), and removal of solvent gave *unsym*-tetraphenylethane (6.2 g, 91%, mp 141–143 °C) from petroleum ether.[24]

Reaction of Benzhydryl Fluoride with Benzhydryllithium. Benzhydryllithium (0.02 mol) in THF (100 ml) at 0 °C was treated dropwise with benzhydryl fluoride (3.72 g, 0.02 mol) in THF (50 ml) for 1.0 h. After work-up, as described above, *sym*-tetraphenylethane (6.43 g, 96%, mp 218–219 °C) was isolated.[24]

Reaction of Benzyl Fluoride with Benzyllithium. Benzyl fluoride (1.10 g, 0.01 mol) was added in one portion to 0.1 M benzyllithium (0.01 mol) in ether (100 ml) and stirred for 20 min when the carbanion color disappeared. After work-up as described above bibenzyl (1.73 g, 95%, mp 50–51 °C) was isolated.[24]

Pentaphenylethane from Trityllithium and Benzhydryl Halides. Benzhydryl bromide (3.55 g, 0.0143 mol) in THF (25 ml) was added dropwise to trityllithium (0.0143 mol) in THF (100 ml) at 0 °C. Upon completion of the bromide addition, the red color of the carbanion disappeared. After work-up as described above for pentaphenylethane, 5.58 g, 95%, mp 157–161 °C (lit.[25] mp 159–166 °C) of hydrocarbon was secured in two crops.[24]

Anal. Calcd for $C_{32}H_{26}$: C, 93.65; H, 6.35. Found: C, 93.37; H, 6.44 and C, 93.33; H, 6.48.

Run 2: A similar experiment using benzhydryl chloride (2.71 g, 0.014 mol) gave pentaphenylethane (5.31 g, 91%).

Pentaphenylethane from Trityllithium and Benzhydryl Tosylate. To a slurry of benzhydryl tosylate[26] (6.48 g, 0.02 mol) in dry ether (100 ml) at 0 °C trityllithium (0.02 mol) in THF (100 ml) was added. The trityllithium lost its color instantly. Addition of H_2O (100 ml) and ether (100 ml) was followed by drying (Na_2SO_4) and removal of the ether solvents to give pentaphenylethane (7.38 g, 90%, mp 155–160 °C).

Reaction of Benzyl Chloride and Trityllithium. Trityllithium (0.02 mol) in THF (100 ml) at 0 °C reacted with benzyl chloride (2.52 g, 0.02 mol) during 15 min required for the addition of the halide to give *unsym*-tetraphenylethane (6.35 g, 95%, mp 143–145 °C).[24]

Reaction of Benzhydryl Chloride and Benzhydryllithium. Benzhydryllithium (0.0305 mol) in THF (100 ml) at 0 °C reacted with benzhydryl chloride (6.19 g, 0.0305 mol) in THF (25 ml) during 15 min required for dropwise addition of the halide to produce *sym*-tetraphenylethane (10.2 g, 100%, mp 218–219 °C from benzene.[24]

Reaction of Lithium Naphthalene with an Equimolar Mixture of Trityl Fluoride and Benzhydryl Fluoride. To an equimolar solution of trityl fluoride (2.623 g, 0.010 mol) and benzhydryl fluoride (1.860 g, 0.010 mol) in THF (30 ml) was added dropwise lithium naphthalene (0.02 mol) in THF (36 ml) during 20 min. After stirring for 24 h the mixture was hydrolyzed and *sym*-tetraphenylethane (0.45 g, 27%, mp 194–197 °C) was isolated. NMR analysis and thin-layer chromatography showed the presence of less than 5% of pentaphenylethane.

Reaction of Lithium Naphthalene with an Equimolar Mixture of Benzhydryl and Benzyl Fluorides. To an equimolar solution of benzhydryl fluoride (1.860 g, 0.010 mol) and benzyl fluoride (1.100 g, 0.010 mol) in dry THF (20 ml) lithium naphthalene (0.020 mol) in THF (44 ml) was added dropwise during 20 min. After stirring for 18 h, hydrolysis with saturated NH_4Cl, extraction into ether (2 × 50 ml), and drying, quantitative GC analysis revealed a 38% yield of dimer coupling products consisting of 69.2% 1,1,2-triphenylethane, 22.5% *sym*-tetraphenylethane, and 8.3% bibenzyl.

Run 2: Following the procedure described above, 0.02 mol of equimolar benzhydryl and benzyl fluorides was treated with an insufficient amount of lithium naphthalene (0.01 mol). GC analysis (10% SE 30 on Chromosorb W-DMCS, 6-ft column) showed a 52% yield of dimers consisting of 75.4% 1,1,2-triphenylethane, 6% *sym*-tetraphenylethane, and 18.6% bibenzyl.

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Cheletropic Reactions of Fluorocarbenes with Norbornadienes

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Abstract: The reaction of difluorocarbene (generated at 20–25 °C) with norbornadiene (**1**) and its 7-methyl derivative (**6**) proceeds initially to give the 1:1 adducts arising from exo and endo 1,2 addition and more importantly from homo-1,4 addition. From an investigation of the thermal behavior of the 1,2 adducts, it is established that the homo-1,4 adducts arise directly from linear cheletropic reaction, thereby constituting an unprecedented example. The 1,2 adducts are cis-fused cyclopropanes and exhibit two mechanistically different types of rearrangement on heating. At 80 °C the endo 1,2 difluorocarbene adduct of **1** smoothly epimerizes to the exo 1,2 adduct. The latter on stronger heating at 225 °C undergoes intramolecular cycloaddition in two steps to give the corresponding tetracyclic structure. The 1,2 adducts derived from fluorochlorocarbene and **1** display an unusual dichotomy of thermal behavior which depends on the configuration of the halogen substituents. Both exo and endo *Z* adducts (**12** and **15**), the more congested isomers, undergo spontaneously the cyclopropyl-allylic rearrangement in which the chlorine substituent migrates. Isomer **12** gives *exo*-4-chloro-3-fluorobicyclo[3.2.1]octa-2,6-diene (**13**), whereas **15** gives the endo ring enlarged product (**16**). In contrast, the exo and endo *E* adducts (**11** and **14**) are more thermally resistant, but at 200 and 100 °C they give stereospecifically **16** and **13**, respectively. This latter behavior is interpreted in terms of an initial stereomutation of the cyclopropane ring which puts the electronically better chlorine substituent in the correct configuration for electrocyclic ring opening. A discussion of the cheletropic reactions and the rearrangements of the cyclopropane adducts is presented. The different requirements for cyclopropane stereomutation and intramolecular cycloaddition are analyzed and discussed.

Introduction

We reported recently that the reaction of difluoro- and fluorochlorocarbene with norbornadiene gave sizable amounts of the endo homo-1,4 adducts.[1] The novelty and mechanistic importance of these results resides in the possibility that they constitute singular and unprecedented examples of linear cheletropic reactions of σ^2 carbenes. In this paper we now demonstrate that the homo-1,4 adducts arise directly and do not derive from any of the 1,2 adducts. By examining the individual thermal behavior of the 1,2 adducts, we elucidate the stereochemical course of their rearrangement and further show that the presence and configuration of the fluorine substituent exert a subtle control over the ease and manner of the opening of the cis-fused cyclopropane ring.

Our chief reason for choosing difluorocarbene was based on the primitive notion that, as difluorocarbene is less electrophilic than the other halocarbenes, the chances were good that reaction with a suitable conjugated diene would reveal some 1,4 addition.[2] It was assumed that the 1,2 and 1,4 additions would be in formal competition, but for different parts of the diene (Figure 1).[3] Both theoretical and experimental studies amply attest to the electrophilic behavior of σ^2 halocarbenes on 1,2 addition.[2,4] Indeed, the best description of the transition state for cyclopropanation is the one in which the carbene with its ligands projecting forward makes a lateral approach to the midpoint of the double bond so that overall C_s symmetry is maintained.[5] The corollary is that the p_z orbital of the carbene is engaged with the π system of the olefin in a nonlinear approach (Figure 2). Consequently any feature in the carbene, or in the substrate for that matter, which would disfavor this particular mode, could call forth 1,4 addition. Moreover, a concerted 1,4 addition, as it is a linear cheletropic reaction, will necessarily entail the simultaneous involvement of the empty and doubly occupied orbitals of the carbenic carbon atom. In this mechanistic context the terms electrophilic and nucleophilic become redundant; thus a carbene, less electrophilic with respect to 1,2 addition, might reveal greater potential for 1,4 addition.

Subsidiary, but nonetheless important, considerations which indicated difluorocarbene were the strength of the carbon–fluorine bond, the small size of the fluorine substituent and its spectroscopic visibility.[6] Difluorocarbene should experience little steric discrimination on approach to an obstructed olefin and once attached, it should stay intact as such and act as a structure probe by virtue of its ^{19}F nuclear magnetic resonance spectrum.

The choice of norbornadiene, a fortunate one as it turned out, was dictated by its suitability as a simple, rigid homoconjugated diene and by its proven ability to undergo [2 + 2 + 2] cycloadditions.[7]

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